



Study of an energy-integrated biodiesel production process using supercritical methanol and a low-cost feedstock



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ABSTRACT

The supercritical biodiesel production process has some disadvantages such as: high reaction temperature, large molar methanol-to-oil ratios (R) and large energy consumption. To mitigate these problems, an energy integrated process in which biodiesel is obtained in a continuous tubular reactor operating at a reaction temperature of 280 °C, R = 20, a residence time of 1 h and a pressure of 110 bar, is proposed. A low-cost lipid feedstock (chicken oil) was used as raw material for testing the process. The enthalpy content of the stream exiting the supercritical reactor was used to eliminate the unreacted methanol in an adiabatic flash drum. The operating conditions of the adiabatic flash were optimized to meet the specification of water and methanol content in the biodiesel phase and minimize the ester and acid content in the vapor phase. These conditions were: P = 0.1 bar and T = 178 °C. For these conditions the methanol content is 88–90% in the vapor phase and lower than 0.2% in the biodiesel phase. A scheme was developed for an energy integrated process maximizing the heat recovery. Composition, temperature and pressure of the streams were determined and also the amount of heat exchanged in each unit. In order to fulfill the quality restrictions the final content of FFA in the biodiesel product had to be further adjusted by adsorption over bleaching silica.

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1. Introduction

Biodiesel is a renewable fuel [1] generally comprising a mixture of fatty acid methyl esters that is produced by reacting glycerides from biomass, such as animal fats or vegetable oils, with an alcohol, usually methanol [2], in the presence or not of a catalyst.

Transesterification with homogeneous strong alkali catalysts is the most widely used industrial technique for producing biodiesel because of some advantages such as a shorter reaction time, higher conversion rate, and a smaller amount of catalyst, as compared to other catalytic processes [3,4]. On the other side, the so-called supercritical method does not use any catalyst [5]. The supercritical method has from the beginning been associated to short reaction times (a few minutes). In order to have a high reaction rate, high methanol-to-oil ratios are employed, that lead to high pressures, elevated energy costs (high reaction temperature) and the need to recycle the large excess of unreacted methanol [6]. These problems severely restrict the supercritical method for the industrial production of biodiesel and there are no commercial biodiesel production facilities currently using the supercritical method. This is partly due to the high energy needed to run the reactor at high temperature and pressure and sustain the supercritical state. In this sense the means to achieve the recycle of high-temperature and high-

pressure methanol is a key factor for solving the problem of high energy consumption and high production cost [7]. However many advantages of the supercritical process should be acknowledged, the main one being the ability to process low quality feedstocks. This is especially important because the price of biodiesel depends 80–90% on the value of the lipidic raw feedstock used.

Of all possible low-cost feedstocks, chicken oil obtained from the steam autoclave treatment of chicken viscera is a feedstock worth to be considered for biodiesel production. It has a major composition of oleic acid methyl ester which is an advantage in comparison with some vegetable oils. Important biodiesel properties such as the oxidation stability, cloud point and cetane number are improved using this raw material.

One important aspect of the biodiesel process is that the net yield of fatty acid methyl esters must be high enough for making the process competitive [8]. As alkaline catalysts are very sensitive to water and free fatty acids (FFA) the percentage of water and FFA in the feedstocks of alkali-catalyzed reactors must be lower than 0.06% (w/w) and 0.5% (w/w), respectively. Otherwise the ester yield is decreased by side reactions during the catalytic transesterification reaction. In the case of the supercritical method the FFA and water contents have no negative effect on the reaction rate or the ester yield. Moreover water and FFA can give impetus to the reaction under certain conditions. For instance chicken oil and frying oil with very high FFA and water contents have been reported to be easily transformed into biodiesel with supercritical methanol [9].

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The objectives of this work are many: (i) Study the properties of biodiesel produced by supercritical transesterification of a high acidity, low cost raw material (chicken oil). (ii) Elucidate the network of chemical reactions taking place in the supercritical reactor with the aid of chromatographic compositional data and a thermodynamic analysis. (iii) Propose a process layout of low energy consumption that enables the production of biodiesel technically compliant with the quality standards. The process synthesis effort will be aided by computer simulation of the reactor, the separation units and the heat exchangers. A mathematical optimization will be performed for minimizing the energy consumption of the process.

Particularly the conditions are studied in which the enthalpy of the reactor product stream is high enough for eliminating residual methanol and water in adiabatic flash drums; at least in an amount sufficient for reaching the limit content values of quality norms. Adiabatic flash drums should enable big energy savings and reduce the heat load of the process. After verifying the validity of the use of adiabatic flash stages a process layout will be proposed using units for reaction, separation and heat recovery. After this, additional steps could be needed for adjusting the final content of the impurities to the desired level. This will be preferentially done by using adsorption units as proposed elsewhere [9].

In comparison to other published reports the current work is a proposal of an energy-integrated process using milder reaction conditions, i.e. lower methanol-to-oil ratio, temperature and pressure. This translates into savings in pumping, methanol recycling and heating/cooling. Another difference is that adsorption instead of washing is chosen as unit operation for adjusting impurity levels in the produced biodiesel. This should lead to a reduction in the volume of generated wastewater and the cost of wastewater treatment and disposal.

2. Materials and methods

2.1. Materials

Chicken oil (24.0% free fatty acids (FFA); 75.8% triglycerides (TG), 0.12% water, 100 iodine value, 33 cSt viscosity) was supplied by Granjas Carnave S.A. (Esperanza, Argentina). This product was obtained by steam autoclave treatment of chicken viscerae. Methanol (>99.9%) was supplied by Dorwil.

2.2. Transesterification reaction

Oil and methanol were placed in a stainless steel autoclave reactor of 50 mL having a thermocouple and a pressure gauge. The amounts of oil and methanol were regulated in order to yield a value of the molar methanol-to-oil ratio (R) of 20. After charging the reactor, the top flange was put and tightened, nitrogen was introduced for purging and all valves were closed. Then the reactor was heated from room temperature to the target temperature (280 °C) at a heating rate of 30 °C min⁻¹. The mixture was allowed to react at the autogenous pressure of the closed system (110 bar) for 1 h. Then the reactor was rapidly transferred to an ice bath to quench the reaction. Once the reactor was cold the top flange was removed and the liquid content was transferred to an Erlenmeyer. The oil was weighed to determine the liquid yield of the reaction. The amount of light gases formed was determined from a mass balance. Reaction tests were performed in triplicates in order to decrease the experimental error. A more detailed description of the used equipment and procedure can be found elsewhere [8].

2.3. Refining steps and tests for methanol balance

The liquid product mixture was first transferred to an atmospheric distillation apparatus. The column was entirely made of Pyrex glass and comprised a spherical reboiler, a multilobe column and a Liebig

condenser. These parts and the heating and cooling units were built according to the ASTM D86 standard. A reboiler temperature of 100 °C, a condenser temperature of 20 °C and a distillation time of 1 h were used to separate the unreacted methanol and other volatile compounds from the rest of the biodiesel phase. The recovered methanol solution and the distilled biodiesel were then weighed separately. The biodiesel phase was left unstirred for 6 h to allow the glycerol phase, if not completely decomposed, to decant to the bottom of the flask as a separate layer. The upper biodiesel layer was then sampled for analysis.

Unreacted methanol separated by the above distillation procedure was analyzed by gas chromatography in a Varian 3800 equipped with a mass spectrometry Saturn 2000 detector.

2.4. Analysis of biodiesel

Samples of biodiesel were analyzed according to different standard techniques as indicated by the quality norms [10,11]. Maximum allowed values as well as the results, are indicated in Table 1.

2.5. Process simulation

The proposed energy integrated biodiesel production process with the involved units is depicted in Fig. 1.

The whole process was simulated using the software UNISIM DESIGN 349. For calculation purposes almost all process units were considered to operate in a continuous fashion. Serial tank bleachers, operated in discontinuous mode, were simulated separately using Matlab for Windows R2013b.

The conditions and composition of the stream entering the expansion valve (VLV-1) were determined taking experimental results into account. The inlet temperature was not fixed and was a variable of the optimization procedure. The simulation methodology involved varying the pressure drop in the inlet valve and obtaining different pressure, temperature and composition values at the exit of the drum.

The flash drum was modeled on the basis of classical liquid–vapor equilibrium. Physical property data of the involved compounds (methanol, glycerol, water, etc.) were taken from the UNISIM property libraries. With respect to the methyl esters, methyl oleate was taken as a model compound for representing biodiesel. Hydrogen and carbon dioxide were the only gaseous compound considered. The thermodynamic properties were estimated using group contribution properties [12].

Due to the presence of highly polar compounds such as methanol and glycerol, and the widely different size of some molecules in the mixture, the solutions were non-ideal. This non-ideality was accounted for by means of activity coefficients. The activity of the compounds in the liquid phase was described using the NRTL (non-random two liquid) or the UNIQUAC (universal quasi-chemical) models. The vapor–liquid

Table 1

Physical and chemical properties of the raw biodiesel obtained by transesterification of chicken oil. Reaction conditions: 280 °C, 110 bar, methanol-to-oil molar ratio, 20.

| Property | Norm method | Norm values | Experimental values |
|--|-------------|-------------|---------------------|
| Methyl ester content, % (w/w) | EN 14103 | >96.5 | 97.0 |
| Density at 15 °C, kg/m ³ | EN ISO 3675 | 860–900 | 876 |
| Viscosity at 40 °C, mm ² /s | D445 | 1.9–6 | 5.7 |
| Flash point, °C | D93 | >130 | 163 |
| Sulfated ash, % (w/w) | D874 | <0.02 | 0.015 |
| Conradson carbon, % (w/w) | D4530 | <0.05 | 0.02 |
| Water content, mg/kg | D2709 | <500 | 800 |
| Free fatty acid content, % | D664 | <0.40 | 2.7 |
| Iodine value | EN 14111 | <120 | 100 |
| Methanol content, % (w/w) | EN 14110 | <0.2 | 0.15 |
| Free glycerol, % (w/w) | D6584 | <0.02 | 0.019 |
| Total glycerol, % (w/w) | D6584 | <0.24 | 0.17 |

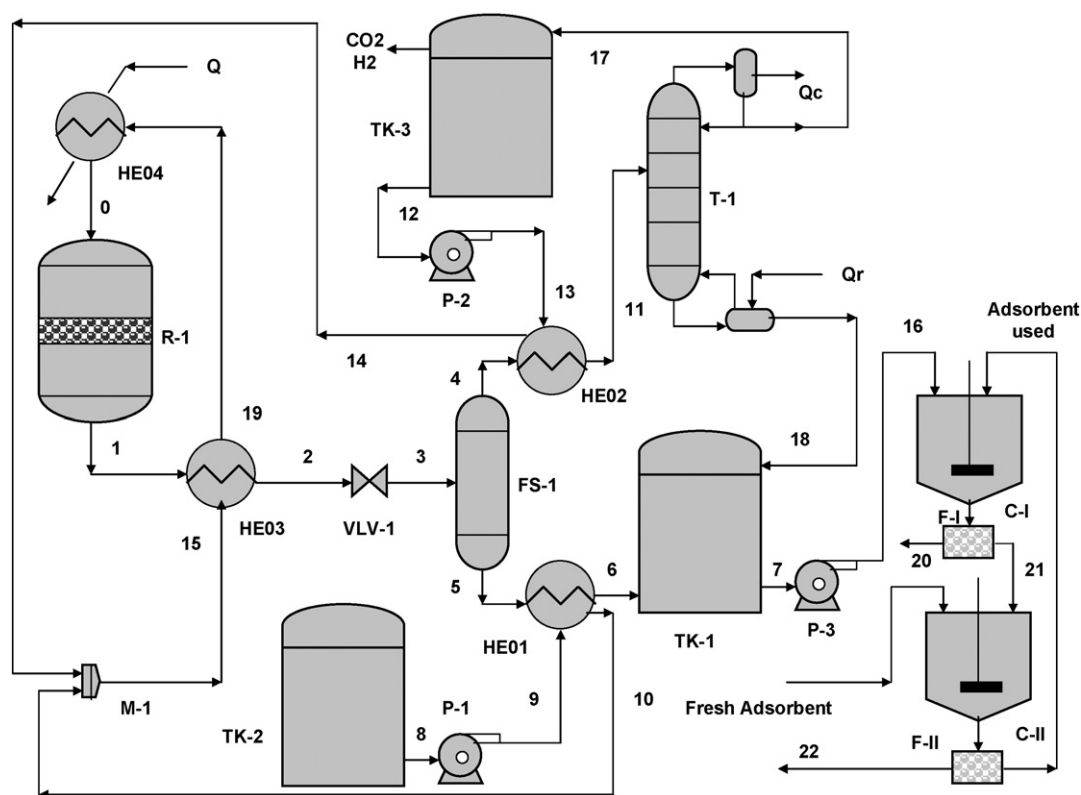


Fig. 1. Flowsheet of a heat integrated process for the production of biodiesel using supercritical methanol. Equipment list: HE01, HE02, HE03: shell and tube heat exchangers. HE04: heater. R-1: tubular adiabatic reactor. VLV-1: expansion valve. FS-1: adiabatic flash drum. T-1: distillation column. C-I, C-II: contactors. F-I, F-II: filters. TK-1: biodiesel buffer tank. TK-2: oil storage tank. TK-3: methanol storage tank. P1, P2, P3: pumps. M-1: streams mixer.

equilibrium was described by means of a combination of the NRTL and SRK (or Peng–Robinson) models. The activity coefficients that could not be modeled with the previous methodology were calculated with the UNIFAC-VLE method [13].

Modeled process units were the flash drum (FS-1), the expansion valve (VLV-1), the heat exchangers (HE01–HE04) and the distillation column (T-1).

The bleaching tanks were simulated using an ad-hoc program written in Matlab for Windows. An LDF (linear driving force) model for mass transfer between the liquid and solid phases was adopted, along with a linear isotherm for the adsorption of the FFAs [14]. The values of the LDF constant ($K = 0.024 \text{ min}^{-1}$) and adimensional Henry's constant for adsorption ($H = 38$) were taken from our previous contribution and correspond to the measured values for adsorption of oleic acid over a commercial silica adsorbent (TriSyl 3000, W.R. Grace & Co.) at a conveniently chosen temperature [14].

3. Results and discussion

3.1. Transesterification reaction

Several transesterification reaction tests were performed at the conditions indicated in Section 2.2. The results indicated that:

- 1) No glycerol appeared as a separate fluid phase. GC analysis indicated that negligible amounts of glycerol were present among the reaction products.
- 2) The mass balance of each reaction test indicated that during the reaction the liquid phase (including the reaction products and the unreacted methanol) suffered a mass loss. This mass balance was performed taking into account the liquid products at room

temperature and for this reason the loss can be attributed to the formation of some compounds that are volatile vapors at room temperature. This loss was on average 2.5% of the initial liquid mass loaded to the reactor.

- 3) The specific consumption of methanol, calculated as the difference between the loaded and recovered mass (after distillation), was equal to 4 mol of methanol (MeOH) per mol of triglycerides (TG). This value was greater than the theoretical stoichiometric value of 3 that corresponds to the regeneration of the 3 OH groups of glycerol.

Table 1 shows the properties of the biodiesel obtained after the elimination of residual methanol. The results indicate that the biodiesel produced complies with most of the quality requirement of the technical norms, except those related to water and free fatty acid (FFA) content.

During the production of biodiesel by the classical alkaline method a stoichiometric amount of 10% glycerol by-product is obtained. The analysis of the product mixture of the supercritical reactor however discloses very low contents of free and total glycerol. These values are lower than the maximum values established by the quality norms. From a process synthesis point of view this means that in the supercritical method costly equipment for residual glycerol removal, like washers and decanters, can be spared.

With the supercritical technique practically no glycerol is obtained as a by-product. It can be supposed that as soon as it is formed glycerol reacts with other compounds in the reactor or is decomposed forming compounds of lower molecular weight [9,15,16]. In this sense many lateral reactions other than transesterification of glycerides and esterification of FFA seem also to occur in the supercritical reactor. These will be analyzed from a thermodynamic point of view in the next section.

3.2. Thermodynamics of the reactions in supercritical methanol

A literature search was performed in order to list all possible reactions occurring in the supercritical reactor [17,18]. For the group of selected reactions the thermodynamic equilibrium constants were calculated from an estimation of the Gibbs free energy by the Joback's group contribution method [12]. A total of 27 reactions are listed in Table 2, including transesterification, hydrolysis, esterification, dehydration, hydrogenation, glycerol reforming, decarboxylation and methoxylation.

The data of Table 2 were generated with disregard of any effect of solvation or interaction with supercritical methanol. This is a necessary approximation, since no information is available to account for these effects. With respect to the estimated thermodynamic values the following comments can be made.

1. The reactions of transesterification of glycerides (reactions 1, 2 and 3) and the reaction of esterification of FFA (9) are all equilibrium limited. The global reaction of transesterification (4) has a thermodynamic equilibrium constant equal to about 0.11. Something similar occurs with the reactions of hydrolysis of glycerides (5, 6 and 7).

2. The reactions of dehydration (11, 12, 17 and 18), etherification (13–16) and reforming of glycerol (19) are thermodynamically feasible. In contrast the formation of polyglycerols (10) is scarcely feasible.

3. Reactions (11) and (12) produce water, acrolein and acetol, all of them in the liquid state at room temperature.

4. Other reactions favored to a great extent are those of decarboxylation of FAME and FFA, that lead to the formation of light gases (CO₂ and CH₄) and long chain alkenes (reactions 23 and 24).

5. The reactions of methoxylation are not very much thermodynamically favored (25, 26 and 27).

3.3. Analysis of residual methanol phase recovered by atmospheric distillation

The survey of products of decomposition that would confirm the occurrence of lateral reactions, was made by GC–MS. The task was complicated in the case of the analysis of the biodiesel phase because this was a complex mixture of many compounds. For this reason the analysis was restricted to the products in the methanol polar phase, that was more amenable for analysis.

Table 2

Thermodynamic analysis of the possible reactions involved in the process of transesterification in supercritical methanol.

| Type of reaction | Chemical reaction | | K _e (280 °C) | ΔG (280 °C) (J/mol) |
|-----------------------|--|------|---------------------------|---------------------|
| Transesterification | TGly + MeOH ⇌ DGly + FAME | (1) | 2.0619 | −3334.72 |
| Transesterification | DGly + MeOH ⇌ MGly + FAME | (2) | 2.0637 | −3338.72 |
| Transesterification | MGly + MeOH ⇌ Gly + FAME | (3) | 2.531 · 10 ^{−2} | 16941.69 |
| Transesterification | TGly + 3 MeOH ⇌ 3 FAME + Gly | (4) | 1.077 · 10 ^{−1} | 10268.24 |
| Hydrolysis | TGly + H ₂ O ⇌ DGly + FFA | (5) | 10.6036 | −10881.07 |
| Hydrolysis | DGly + H ₂ O ⇌ MGly + FFA | (6) | 10.6128 | −10885.07 |
| Hydrolysis | MGly + H ₂ O ⇌ FFA + Gly | (7) | 1.302 · 10 ^{−1} | 9395.34 |
| Hydrolysis | TGly + 3 H ₂ O ⇌ 3 FFA + Gly | (8) | 14.6504 | −12370.81 |
| Esterification | FFA + MeOH ⇌ FAME + H ₂ O | (9) | 1.9445 · 10 ^{−1} | 7546.35 |
| Dehydration | 2 Gly ⇌ Di-Gly + H ₂ O | (10) | 1.3869 · 10 ^{−1} | 3334.17 |
| Dehydration | Gly ⇌ Acrolein + 2 H ₂ O | (11) | 1.527 · 10 ¹² | −129282.66 |
| Dehydration | Gly ⇌ Acetol + H ₂ O | (12) | 1.7312 · 10 ¹¹ | −119249.94 |
| Etherification | Gly + MeOH ⇌ Gly-O-Me + H ₂ O | (13) | 1.792 · 10 ³ | −34522.32 |
| Etherification | Gly-O-Me + MeOH ⇌ Gly-(O-Me) ₂ + H ₂ O | (14) | 22.01 | −14247.01 |
| Etherification | Gly-(O-Me) ₂ + MeOH ⇌ Ether Glycerol + H ₂ O | (15) | 22.02 | −14248.57 |
| Etherification | Gly + 3 MeOH ⇌ Ether Glycerol + 3 H ₂ O | (16) | 8.6881 · 10 ⁵ | −63017.90 |
| Dehydration | Gly-(O-Me) ₂ ⇌ (O-Me) ₂ CH-CH=CH ₂ + H ₂ O | (17) | 2.577 · 10 ²⁷ | −290859.20 |
| Dehydration | 2 MeOH ⇌ Me-O-Me + H ₂ O | (18) | 10.4609 | −10818.64 |
| Reforming of glycerol | Gly + 3 H ₂ O ⇌ 3 CO ₂ + 7H ₂ | (19) | 4.4879 · 10 ²¹ | −229749.67 |
| Hydrogenation | Acrolein + H ₂ ⇌ Aryl Alcohol | (20) | 7.0736 | −9015.56 |
| Hydrogenation | Acetol + H ₂ ⇌ Acetone + H ₂ O | (21) | 10.4609 | −97385.72 |
| Decarboxylation | Acetol ⇌ Acetaldehyde + CO + H ₂ | (22) | 6.2151 · 10 ⁴ | −50863.3 |
| Decarboxylation | FFA ⇌ Alkene + CO ₂ | (23) | 5.0372 · 10 ⁶ | −71116.9 |
| Decarboxylation | FAME ⇌ Alkene + CO ₂ + CH ₄ | (24) | 5.1842 · 10 ¹³ | −145526.4 |
| Methoxylation | Alkene + MeOH ⇌ Methoxy Comp. | (25) | 8.3298 · 10 ^{−3} | 22064.1 |
| Methoxylation | Alkene + 2 MeOH ⇌ Methoxy Comp. 1 | (26) | 1.4792 · 10 ^{−5} | 51250.8 |
| Methoxylation | FAME + MeOH ⇌ Methoxy Compound 2 | (27) | 9.0727 · 10 ^{−2} | 11059.44 |

TG: Triolein (Triglyceride).

DG: Diolein (Diglyceride).

MG: Monoolein (Monoglyceride).

FAME: Methyl oleate (biodiesel). CH₃(CH₂)₇CHCH₂O(CH₂)₇CH₂COOCH₃.

MeOH: Methanol.

H₂O: Water.

FFA: Oleic acid.

Gly: Glycerol.

Di-Gly: Di-glycerol.

Gly-O-Me: glyceryl-methyl-ether.

Alkene: Alkene from FAME: CH₃(CH₂)₇CH=CH-(CH₂)₅CH=CH₂.

Methoxy comp.: methoxylated compound produced by methoxylation of the alkene.

CH₃(CH₂)₇CH-CH₂O(CH₂)₆CH=CH₂.

Methoxy comp. 1: methoxylated compound produced by methoxylation of the alkene.

CH₃(CH₂)₇CHCH₂O-(CH₂)₆CHCH₂OCH₃.

Methoxy comp. 2: methoxylated compound produced by methoxylation of the FAME.

CH₃(CH₂)₇CHCH₂O-(CH₂)₇CH₂COOCH₃.

Analysis of the recovered methanol by GC–MS using the technique described in Section 2.3 showed the presence of the following compounds: acetol ($C_3H_6O_2$), acetone (C_3H_6O), dimethyl acetal ($C_5H_{10}O_2$). The concentration of these compounds in the methanol phase was 0.1–0.2% (mass basis). The residual glycerol content was about 4–5 ppm. Acetol, acetone and dimethyl acetal were absent in the fresh methanol used in the reaction; even at the trace level. Acetol has a boiling point of 145.7 °C at atmospheric pressure therefore it can be expected that a portion thereof will leave the biodiesel phase together with methanol during the distillation step. The presence of acetol would be justified by reaction (12) that is highly favored thermodynamically. The presence of acetone would be justified by equation (21) (acetol hydrogenation), also thermodynamically favored. Hydrogen for this reaction could come from the occurrence of reactions (19) and/or (22). Reaction (22) can be discarded because no acetaldehyde was detected (20.2 °C boiling point) in the recovered methanol. Acetone has a boiling point of 56 °C and therefore it was probably completely eliminated during the distillation step. Since only very little amounts were collected the occurrence of this reaction can be disregarded.

Acrolein has a boiling point of 57 °C. However no acrolein was detected in the recovered methanol phase. Therefore the occurrence of reaction (11) should be discarded in spite of being thermodynamically feasible.

The weight loss seen in the tests can therefore be explained by the occurrence of some of the following reactions.

1. Reaction (19) leading to the formation of CO_2 and H_2 .
2. Reactions (23) or (24) of decarboxylation of FAME and FFA that are very much thermodynamically favored (reactions (23) and (24)).
3. Reaction (18) involving the formation of dimethyl ether and water. Such ether has a boiling point of -24 °C. This reaction would justify the greater specific consumption of methanol detected in the transesterification tests. Other thermodynamically feasible reactions that could cause the great consumption of methanol could be those of etherification of glycerol to mono-, di- and trimethyl ethers (reactions (13), (14), (15) and (16)).

The presence of dimethyl acetal in the methanol phase should be highlighted. This product is formed by means of the dehydration of dimethyl glycerol to dimethyl acetal (17), a reaction much favored thermodynamically. Dimethyl acetal has a boiling point of 64.7 °C and therefore it should be distilled off with methanol during the distillation step.

As previously indicated only small amounts of glycerol dimethyl ether were found and hence reaction (14) is marginal. Reactions (14), (15) and (17) can then be discarded and it can be supposed that only monomethyl glycerol ethers are formed.

The greater consumption of methanol cannot be explained by the occurrence of the methoxylation reactions (25)–(27) because they are only scarcely feasible. If they occurred, a decrease of the iodine index of biodiesel in comparison to the parent raw material should be found. However this does not happen (see Table 1).

From the GC–MS results it can be concluded that many lateral reactions occur besides those of transesterification and esterification. (4), (8), (9), (12), (13) and (19) are possible reactions. Decarboxylation reactions (23–24) though thermodynamically possible do not seem to occur. According to the experimental evidence they need higher temperatures and longer reaction times to proceed to a meaningful extent [9,15,16,19].

Taking into account the laboratory tests we can finally conclude that the compounds needed to be eliminated downstream the supercritical reactor are water, FFA, methanol, other liquids and gaseous products.

3.4. Simulation of the adiabatic flash drum

The conditions and composition of the stream entering the flashing valve (VLV-1) of the adiabatic drum are indicated in Table 3.

The working conditions had to be optimized with the following requirements.

1. Obtaining a liquid phase (biodiesel) complying the quality restrictions on residual water and methanol.
2. Minimizing the FAME and FFA contents in the methanol-rich vapor phase.
3. Maximizing the heat recovery.

The elimination of the excess methanol makes use of most of the heat content of the inlet stream. Fig. 2 shows a plot of the content of methanol in the liquid stream leaving the flash drum, as a function of the temperature of equilibrium of the flash tank, for different values of the operation pressure (at adiabatic conditions). The results indicate that as the pressure in the flash drum is increased the content of methanol in the liquid phase also increases. A similar effect occurs when the equilibrium temperature of the flash drum is decreased. For a gauge pressure of 0.1 bar (1.1 absolute bars) and equilibrium temperature values in the range 178–188 °C, a biodiesel is obtained that has residual methanol contents lower than 0.2% (ASTM technically compliant).

Fig. 3 shows plots of the water content in the liquid phase leaving the flash drum, as a function of the equilibrium temperature of the flash drum, and at different values of the operation pressure (adiabatic conditions). The results indicate that as the pressure in the flash drum is increased the water content in the liquid phase also increases. For a gauge pressure range of 0.1–1.0 bar (1.1 to 2.0 absolute bars) and temperatures between 125–188 °C a biodiesel is obtained with a residual water content lower than 0.05% (maximum allowed by the ASTM norm).

The results indicate that the optimal operation conditions are 1.1 bar and 178–188 °C. At these process conditions the biodiesel phase has water and methanol contents below the maximum limits established in the quality norms.

It is however necessary to analyze what happens with the contents of FAME and impurities because they define the quality of the biodiesel fuel leaving the flash drum at 0.1 bar and different temperature values. These results are indicated in Table 4.

It can be seen that as the temperature is raised the water and methanol contents are decreased, and that the FAME and FFA contents are slightly increased. The FFA content is only little affected by the temperature in the analyzed range and varies greatly in comparison to the maximum of the quality norm (0.4%). With respect to the FAME fraction in the liquid phase Table 4 shows that the FAME content in the liquid phase is not modified in the 178–188 °C temperature range with respect to the minimum value established by the norm (96.5%).

In contrast the FAME and FFA contents in the vapor phase increase as the temperature is increased or the pressure is lowered (see Figs. 4 and 5). It can also be seen that if the temperature of the flash drum is increased, a decrease in the methanol content in the liquid phase can be gotten at the expense of greater FAME and FFA contents in the vapor phase. A temperature of 178–188 °C seems therefore the most convenient. At this value the methanol specification is fulfilled and the FAME content in the vapor phase is the lowest. It would be therefore necessary to place a heat exchanger at the exit of the reactor to cool down the stream from 280 °C to 240 °C, temperature at which the stream must enter the expansion valve if the equilibrium value of 178–188 °C is to be reached.

Both the liquid and vapor streams leaving the flash drum have a high enthalpy content that can be employed to preheat the feedstock streams of the process (triglycerides and methanol). After the flash

Table 3
Conditions and composition of the stream entering the flashing valve (VLV-1) of the adiabatic drum.

| Operating conditions | | Mass fraction, % | | | | | | | | | |
|----------------------|---------|------------------|--------|----------|--------|---------|-----------------|--------|--------|---------------|----------------|
| T (°C) | P (bar) | Methanol | Water | Glycerol | FFA | FAME | CO ₂ | Acetol | MGE | Triglycerides | H ₂ |
| 240 | 110.45 | 35.6247 | 0.1399 | 0.01 | 1.7188 | 56.8996 | 2.9979 | 1.479 | 0.7255 | 0.0878 | 0.3168 |

MGE: monoglycerol ether.

drum the vapor stream must enter the distillation column (T-1) in order to recover the methanol and recirculate it to the transesterification reactor (R-1). In this way an efficient heat recovery is gotten.

3.5. Process design

A heat-integrated process flowsheet for the production of biodiesel with supercritical methanol is proposed in Fig. 1. The fatty feedstocks should be filtered and degummed before entering the reactor. These operations are not included in the current lay-out.

In order to select the kind of reactor to be used several points must be taken into account: i) the need for continuous operation; ii) the high values of temperature and pressure of reaction; and iii) the negligible enthalpy change of the transesterification reaction. In attention to these issues the best option is a tubular reactor working under adiabatic conditions (R-1).

For the choice of the reactor conditions a careful analysis must be made. The transesterification of oils and fats for producing biodiesel must proceed almost to completion in order to produce a fuel of adequate quality. Both the ASTM D6751 and EN 14214 norms establish a maximum content of total glycerol (free and combined) of 0.24%. If we consider that all combined glycerol is in the form of unreacted triglycerides and that the concentration of diglycerides and monoglycerides in the biodiesel is negligible, the minimum conversion should be 97.8%, corresponding to a minimum content of methyl ester higher than 96.5% after eliminating unreacted methanol and free glycerol. This high conversion value poses restrictions on the reaction conditions. In most reported supercritical processes a one-stage reaction scheme is used and short reaction times (a few minutes) are considered to be optimal since they lead to high throughputs. However it has been found that longer reaction times (e.g. 1 h) lead to the reforming of glycerol in the supercritical reaction medium effectively eliminating this by-product. Since transesterification is an equilibrium reaction, the use of only one reaction stage with no glycerol degradation demands

the use of high methanol-to-oil ratios, typically 42 on a molar basis, to achieve the desired conversion. Typical temperatures for these “fast reaction” processes are 300–350 °C [20]. For example Goto et al. [5] propose a process in which oils are reacted with supercritical methanol at methanol-to-oil molar ratios higher than 40. Even at these conditions conversion is not complete and the unreacted glycerides must be separated by low pressure distillation in order to be recycled to the reactor. The disadvantages of a high methanol-to-oil ratio are the related high pressure and the high cost for recycling the unreacted methanol. High reaction temperatures, though accelerating the reaction, also produce inconveniently high pressures, and increase the heating and cooling process duties. Too high pressures not only increase the pumping costs, but also the required wall thickness in process vessels and pipes.

Another issue is that of the degradation of the biodiesel. Imahara et al. [15] reported that at severe reaction conditions (350 °C and 43 MPa) polyunsaturated methyl esters suffer extensive decomposition. Conversely at milder reaction conditions, such as 270 °C and 17 MPa, only methyl linolenate is found to undergo cis-trans isomerization, and no decomposition and no loss of liquid yield occurs. These authors [15] conclude that reaction temperatures should be lower than 300 °C and reaction pressures higher than 8 MPa. Similar results have been published by He et al. [16].

These aspects have been analyzed by Manuale [21] who concludes that mild reaction conditions (280 °C, molar methanol-to-oil ratio = 6–20, pressure <10 MPa) are optimal on the basis of low energy consumption, while the resulting reaction times of 0.5–1.5 h are considered to be acceptable. 280 °C and a methanol-to-oil ratio of 20 are used in this work.

The use of adiabatic flash drums (FS-1) to eliminate the unreacted methanol with the aid of the enthalpy content of the product stream is possible. One cooling stage (HE03) is needed before the expansion valve (VLV-1). Special care was taken to avoid the crossing of the temperatures of the streams exchanging heat in the different units and to maximize the heat recovery.

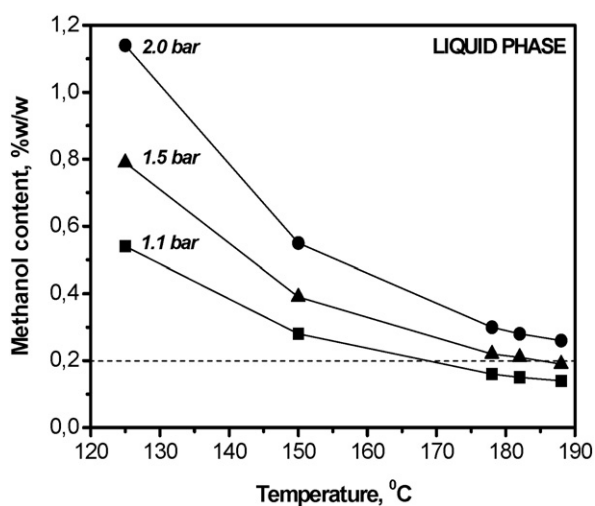


Fig. 2. Residual methanol content in the liquid stream leaving the flash drum, as a function of the operation equilibrium temperature, at different values of the entrance pressure. Horizontal dotted line: maximum value allowed by the EN 14110 norm, 0.2% (w/w).

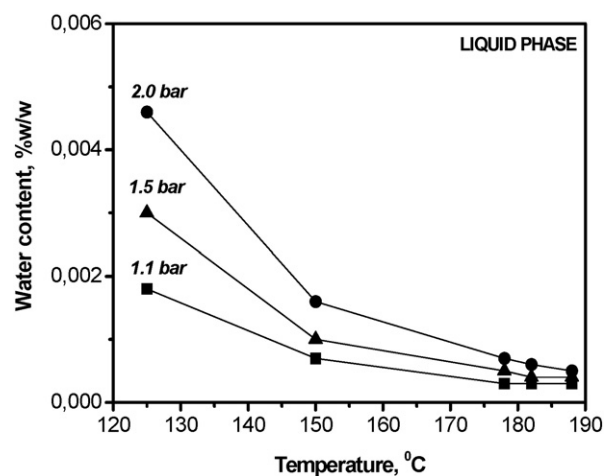


Fig. 3. Water content in the liquid stream leaving the flash drum, as a function of the operation equilibrium temperature, at different values of the entrance pressure. Maximum value allowed by the D2709 norm, 0.05% (w/w).

Table 4

Values of mass composition (water, FAME and FFA) of the liquid fuel stream leaving the adiabatic flash drum (at 1.1 bar and varying equilibrium temperature) as obtained by simulation.

| T° Flash (°C) | MeOH (%) | H ₂ O (%) | FAME (%) | FFA (%) |
|---------------|----------|----------------------|----------|---------|
| 125 | 0.54 | 0.0018 | 95.29 | 2.88 |
| 150 | 0.28 | 0.0007 | 96.16 | 2.91 |
| 178 | 0.16 | 0.0003 | 96.50 | 2.96 |
| 182 | 0.15 | 0.0003 | 96.53 | 2.97 |
| 188 | 0.14 | 0.0003 | 96.55 | 2.98 |

As previously discussed it is necessary to reduce the temperature of the stream exiting the reactor (1) by about 40 °C (from 280 to 240 °C). This can be done in one stage with a heat exchanger (HE03). In order to optimize the heat recovery it is convenient if the streams involved in HE03 are the reactor product stream (1) and the feedstock stream (15). Both streams have been previously preheated in two heat exchangers (HE01 and HE02). The fatty feedstock stream (9) would enter HE01 and exchange heat with the liquid that exits the flash drum (5). The methanol stream (13) would be preheated in HE02, cooling the vapor stream (4) that leaves the flash drum.

In order to heat the mixture of the fatty feedstock and the methanol to the chosen reaction temperature (280 °C) a final stage of heating is needed (HE04) before the reactor. In this case a very hot fluid is needed (300–330 °C). The most suitable option seems to use a thermal oil heater. This system can be easily adapted to this application.

The liquid stream (6) must be sent to the storage tank TK-1. This tank is a buffer vessel that feeds the discontinuous bleaching tanks (C-I and C-II) used for adjusting the final FFA content. These bleachers are operated in a countercurrent liquid–solid flow pattern in order to minimize the use of bleaching adsorbent. In HE02 the vapors being issued by the flash drum (4) are cooled down to the inlet temperature of the distillation column (T-1).

The working pressure of the adiabatic flash drum (FS-1) is dictated by the working pressure of both storage tanks (TK-2 and TK-3), that work at atmospheric pressure, and the pressure drop of the heat exchangers (HE01 and HE02) and the distillation tower (T-1).

Stream (11) leaving HE02 not only contains methanol but also water, FAME and traces of products of decomposition of glycerol that were not considered for the simulation of the flash drum. In order to prevent the accumulation of these compounds in the methanol streams, water traces, FAMES, ketones, aldehydes, paraffins, etc., must be eliminated from the methanol phase before this is recycled. The most convenient technique seems to be the distillation of the product. The methanol is recovered from the head (17) of the column (T-1) while

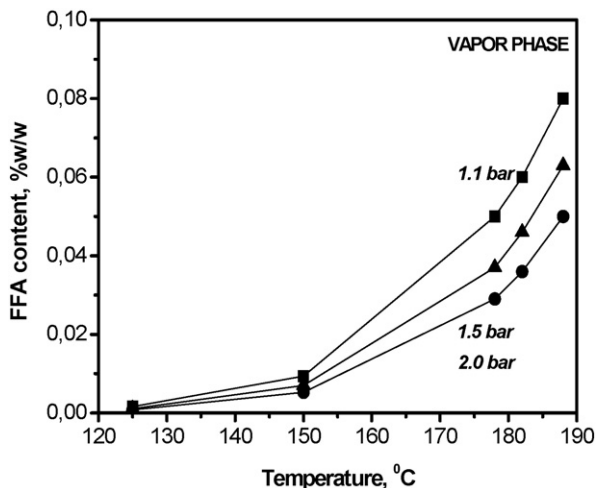


Fig. 4. FFA content in the vapor stream exiting the flash drum, as a function of the operation equilibrium temperature, at different values of the entrance pressure.

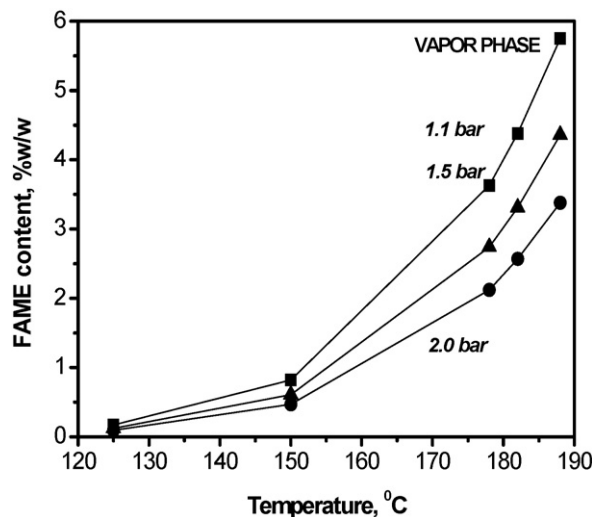


Fig. 5. FAME content in the vapor stream exiting the flash drum, as a function of the operation equilibrium temperature, at different values of the entrance pressure.

the water and the heavier compounds are removed from the bottom. The bottom stream (18), rich in FAMES, ethers and acetol, can be directly sent to the biodiesel pool. With this layout the global economy of the process is improved.

The product stream exiting TK-1 is not fully technically compliant of the biodiesel quality requirements (see Table 1). Its FFA and water contents must be reduced. Its FAME content must be increased. This is achieved in the current process using two serial countercurrent bleachers (C-I and C-II) with their respective filters for separation of the silica adsorbent (F-I and F-II). Silica selectively adsorbs FFA from the biodiesel phase. Removal of water traces in the biodiesel phase occurs in the bleaching tank simultaneously with adsorption because of the temperature and vacuum conditions employed [14,22,23]. In this sense it must be remarked that at 80 °C or slightly higher temperatures water desorption from the adsorbent in the oil only proceeds to a significant degree at vacuum conditions. Fig. 6 shows the results obtained after the simulation of the two countercurrent bleachers.

According to the flowsheet of Fig. 1 the spent adsorbent is retained in filter F-1. It is not implied that the adsorbent is reused though this is indeed possible. In the most simple operation mode the adsorbent is discarded. It was assumed that the cost of the adsorbent did not alter very much the economics of the process. In this sense silica is among the cheapest materials in the adsorbents market. Even in the case of high adsorbent consumption (e.g. 0.07–0.09 g/g) the costs of operating the bleachers should compare favorably against those of washing/drying the biodiesel and treating and disposing of the generated wastewaters.

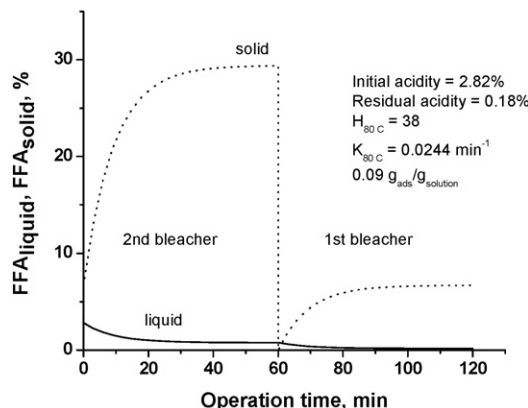


Fig. 6. FFA content in the liquid and solid phases, as a function of the bleaching time.

Table 5

Process conditions (pressure, temperature and mass flow rate) of the different streams of the flowsheet, as obtained by simulation.

| Stream Name | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 22 |
|-----------------------|------|------|-------|------|--------|--------|--------|--------|------|--------|--------|--------|------|--------|--------|--------|--------|--------|-------|--------|---------|
| Temperature (°C) | 280 | 280 | 240 | 182 | 182 | 182 | 75 | 80 | 20 | 30 | 154 | 80 | 20 | 25 | 85 | 114 | 80 | 66.5 | 141 | 150.5 | 80 |
| Pressure (bar) | 111 | 111 | 110.4 | 1.14 | 1.14 | 1.14 | 1.01 | 1.01 | 1.01 | 111.71 | 111.15 | 1.1 | 1.01 | 112.71 | 112.71 | 111.15 | 1.41 | 1.09 | 1.1 | 111.15 | 1.41 |
| Mass Flow Rate (kg/h) | 2000 | 2000 | 2000 | 2000 | 858.71 | 1141.3 | 1141.3 | 1222.6 | 1160 | 1160 | 1160 | 858.71 | 840 | 840 | 840 | 2000 | 1222.6 | 777.42 | 81.29 | 2000 | 1190.32 |

Table 6

Mass composition of the different streams of the process.

| Stream Name | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 22 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|-------|-------|-------|--------|----|----|----|--------|--------|-------|--------|--------|--------|
| Methanol (%w) | 42.025 | 35.625 | 35.625 | 35.625 | 82.765 | 0.156 | 0.156 | 0.147 | 0 | 0 | 0 | 82.765 | 1 | 1 | 1 | 42.0 | 0.147 | 99.93 | 0.030 | 0.42 | 0.152 |
| Water (%w) | 0.104 | 0.140 | 0.140 | 0.140 | 0.325 | 0.0003 | 0.0003 | 0.189 | 0.18 | 0.18 | 0.18 | 0.325 | 0 | 0 | 0 | 0.104 | 0.189 | 0.07 | 2.845 | 0.104 | 0.010 |
| Glycerol (%w) | 0 | 0.01 | 0.01 | 0.01 | 0.023 | 0.0006 | 0.0006 | 0.016 | 0 | 0 | 0 | 0.023 | 0 | 0 | 0 | 0 | 0.016 | 0 | 0.238 | 0 | 0.0164 |
| Free Fatty Acids (%w) | 13.914 | 1.719 | 1.719 | 1.719 | 0.06 | 2.967 | 2.967 | 2.812 | 24 | 24 | 24 | 0.06 | 0 | 0 | 0 | 13.92 | 2.812 | 0 | 0.634 | 13.92 | 0.18 |
| FAME (biodiesel) (%w) | 0 | 56.9 | 56.9 | 56.9 | 4.248 | 96.515 | 96.515 | 93.081 | 0 | 0 | 0 | 4.248 | 0 | 0 | 0 | 0 | 93.081 | 0 | 44.875 | 0 | 95.78 |
| CO ₂ (%w) | 0 | 3.0 | 3.0 | 3.0 | 6.977 | 0.004 | 0.004 | 0.004 | 0 | 0 | 0 | 6.977 | 0 | 0 | 0 | 0 | 0.004 | 0 | 0 | 0 | 0.0041 |
| Acetol (%w) | 0 | 1.479 | 1.479 | 1.479 | 3.240 | 0.154 | 0.154 | 2.419 | 0 | 0 | 0 | 3.240 | 0 | 0 | 0 | 0 | 2.419 | 0 | 34.230 | 0 | 2.484 |
| Ether (%w) | 0 | 0.726 | 0.726 | 0.726 | 1.623 | 0.05 | 0.05 | 1.187 | 0 | 0 | 0 | 1.623 | 0 | 0 | 0 | 0 | 1.187 | 0 | 17.148 | 0 | 1.219 |
| H ₂ (%w) | 0 | 0.317 | 0.317 | 0.317 | 0.738 | 0.0002 | 0.0002 | 0.0002 | 0 | 0 | 0 | 0.738 | 0 | 0 | 0 | 0 | 0.0002 | 0 | 0 | 0 | 0.0002 |
| Triglycerides (%w) | 43.957 | 0.088 | 0.088 | 0.088 | 0 | 0.154 | 0.154 | 0.144 | 75.82 | 75.82 | 75.82 | 0 | 0 | 0 | 0 | 43.976 | 0.144 | 0 | 0 | 43.976 | 0.1513 |

Table 7
Process energy consumption.

| Equipment | Energy consumption (Kw) |
|--------------------------|-------------------------|
| Triglycerides pump (P-1) | 5.38 |
| Methanol pump (P-2) | 4.39 |
| Biodiesel pump (P-3) | 0.02 |
| Heater (HE04) | 267.22 |
| Reboiler column (Qr) | 11.54 |
| Total | 288.55 |

Tables 5 and 6 show a summary of the simulation results for the different process streams. Biodiesel leaving the bleachers (stream 22) fulfills all quality requirements except for the FAME content (95.8 against 96.5%). In the final biodiesel stream there is however a 3.7% contribution due to acetol and ether. These compounds are known as good fuel components and they can be left blended in the final biodiesel product [24–26].

Table 7 shows values of energy consumption of the process units. A total energy consumption of 288.55 kW was found for the proposed flowsheet, for a given biodiesel output flowrate of 1100 kg/h. This means that the average energy consumption is 262 W-h per kg of biodiesel produced for the supercritical process thus outlined. Table 8 contains a comparison of reported values of energy demand for other supercritical processes. It can be seen that the energy consumption of the current supercritical process with heat recovery is similar to that computed by van Kasteren and Nisworo [27] and much smaller than the value reported by Glicic et al. [28], Marulanda [29] and Lee [30]. In the case of the report of Lee [26] simulations were also performed of alkali catalyzed plants with acid preesterification (for waste oil) and with no pretreatment (for fresh oil). This author found that the supercritical process had a higher energy consumption than the alkali catalyzed process but a lower energy consumption than the acid/alkali catalyzed process.

A comparison only on the basis of energy consumption is important but other aspects impacting on the cost should also be considered. For example the cost of the treatment of the process wastewater is usually disregarded in all reports. Marulanda [29] has stressed the much lower potential environmental impact (PEI) of the supercritical process in comparison to that of the alkali-catalyzed process, due to the lower issue of effluents. The subject of the biodiesel wastewater treatment in conventional alkali-catalyzed plants has been fairly well revised [31–34]. The amount of wastewater produced varies between 0.2–1.2 L per liter of biodiesel produced according to Srirangsan et al. [34]. Biodiesel wash water has extremely high biochemical oxygen demand (BOD), total dissolved solids (TDS), glycerin and residual fats, oils and greases (O&G), as well as highly acidic or basic conditions depending on the generating process. Untreated wash water has been found to have concentrations in excess of 63,200 ppm BOD, high concentration of O&G (3160 ppm), with a very basic pH, high methanol and glycerin

content (11,000 and 1370 ppm). These parameters are directly determined by feedstock type and method of processing and can vary greatly both from plant to plant and from batch to batch. According to common sewage regulations, limit values for discharge should be 250 ppm BOD and less than 100 ppm O&G. The amount of treatment needed cannot be overstressed.

Most authors propose the use of biodigestors as the core process unit of the wastewater treatment plant of the alkali-catalyzed biodiesel process. These biodigestors are mostly anaerobic. Before the biodigestors the usual pretreatments include FFA recovery (by acidulation of the soaps), coagulation (chemical or electrostatic) or flotation (with dissolved air) and pH adjustment. After the biodigestors another flotation unit is usually used to remove the suspended biofilm. The digestors are also coupled to scrubbers to reduce unpleasant odors. Most authors coincide in highlighting that the main pollutant contributing to the chemical oxygen demand is methanol and that its abatement in the wastewater treatment plant is incomplete [31–33]. As it can be inferred, wastewater treatment can be cumbersome and costly. In this sense, supercritical, non-catalytic processes need no washing steps, and generate negligible amounts of wastewater. Also unreacted methanol should never appear in the effluent streams because it is practically completely removed from the biodiesel phase of the reactor product and recycled back to the feed.

4. Conclusions

A flowsheet for a heat integrated process for the production of biodiesel with supercritical methanol was proposed. The process was optimized to maximize the heat recovery and is simpler than other catalytic processes. The latter demands a higher number of stages and generate a higher amount of effluents that must be treated before disposal. One key element of the proposed process is the use of the enthalpy content of the product stream leaving the supercritical reactor to eliminate the unreacted methanol in an adiabatic flash drum. The operating conditions of this flash drum were optimized at 178 °C and 0.1 bar with attention to a balance between quality and energy economy issues. In order to fulfill the quality restrictions concerning the final content of FFA, the biodiesel product was further bleached in countercurrent adsorption units. A simulation of the proposed heat integrated process was made using the UNISIM software. Composition, temperature and pressure of the streams were determined, along with the amount of heat exchanged in each unit. The results indicate that the proposed process has an energy duty of 262 W per kg/h of biodiesel product. This is one of the lowest values reported for a supercritical biodiesel production process.

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Table 8
Comparison of energy consumption values reported for different processes of biodiesel production.

| Process type | Ref. | Reactor conditions | | | | Yield ^(b) (%) | Specific energy consumption (kW·h/kg Bio) |
|-------------------|-----------|--------------------|--------|----------------------|-------------------------------------|--------------------------|---|
| | | P (bar) | T (°C) | R _{MeOH/TG} | T _R ^(a) (min) | | |
| SC | This work | 100 | 280 | 20 | 60 | 103 | 0.262 ^(c) |
| SC | 23 | 200 | 400 | 9 | 6–10 | 110 | 0.496 ^(c) |
| SC | 24 | 280 | 280 | 42 | – | 97 | 2.095 ^(c) |
| SC | 25 | 128 | 280 | 24 | 17 | 99.8 | 0.287 ^(d) |
| SC | 25 | 128 | 280 | 24 | 17 | 99.8 | 0.243 ^(e) |
| SC, WVO | 26 | 190 | 350 | 24 | 13.3 | 96 | 0.848 ^(f) |
| SubC, AlkC, FVO | 26 | 4 | 60 | 6 | 60 | 95 | 0.507 ^(f) |
| SubC, AcAlkC, WVO | 26 | 4 | 70/60 | 6 | 60/60 | 100/95 | 1.136 ^(f) |

^(a)T_R: residence time, ^(c)plant of 10,000 ton/year, ^(e)plant of 800,000 ton/year.

^(b)(kg Bio/kg Oil)*100 ^(d) plant of 8000 ton/year ^(f) plant of 40,000 ton/year.

SC = supercritical SubC = subcritical AlkC = alkali catalyzed.

FVO = fresh vegetable oil WVO = waste vegetable oil.

AcAlkC = first stage acid-catalyzed, second alkali catalyzed.

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